

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C25B 11/04	A1	(11) International Publication Number: WO 96/24705 (43) International Publication Date: 15 August 1996 (15.08.96)
(21) International Application Number: PCT/GB96/00157 (22) International Filing Date: 26 January 1996 (26.01.96) (30) Priority Data: 9502665.4 11 February 1995 (11.02.95) GB (71) Applicant (for all designated States except US): IMPERIAL CHEMICAL INDUSTRIES PLC [GB/GB]; Imperial Chemical House, Millbank, London SW1P 3JF (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): HODGSON, David, Ronald [GB/GB]; 7 Grenaby Avenue, Hindley Green, Wigan WN2 4HZ (GB). ROURKE, Francis [GB/GB]; 23 Keats Lane, Wincham, Cheshire CW9 6PP (GB). (74) Agents: THOMAS, Ieuan et al.; ICI Chemicals & Polymers Limited, Intellectual Property Dept., P.O. Box 11, The Heath, Runcorn, Cheshire WA7 4QE (GB).		(81) Designated States: AU, CA, CN, FI, JP, KR, MX, NO, PL, TR, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: CATHODE FOR USE IN ELECTROLYTIC CELL (57) Abstract A cathode wherein the electrocatalytically-active outer layer is of substantially uniform thickness and has contours which are at least substantially the same as the contours of the substrate immediately underlying it. The electrode may be prepared by depositing the electrocatalytically-active outer layer by physical vapour deposition. The electrocatalytically-active outer layer comprises (a) cerium and/or cerium oxide and at least one non-noble Group 8 metal or (b) platinum and/or platinum oxide and ruthenium and/or ruthenium oxide.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

CATHODE FOR USE IN ELECTROLYTIC CELL

This invention relates to a cathode for use in an electrolytic cell, and in particular to a cathode which has a low hydrogen over-voltage when used in the electrolysis of water or brine, eg aqueous alkali metal chloride solutions, and to a method for the
5 preparation of the cathode,

The voltage at which a solution may be electrolysed at a given current density is made up of and is influenced by a number of features, namely the theoretical electrolysing voltage, the over-voltages at the anode and cathode, the resistance of the solution which is electrolysed, the resistance of the diaphragm, if any, positioned between the anode and
10 cathode, and the resistance of the metallic conductors and their contact resistance.

As the cost of electrolysis is proportional to the voltage at which electrolysis is effected, and in view of the high cost of electrical power, it is desirable to reduce the voltage at which a solution is electrolysed to as low a voltage as possible. In the
15 electrolysis of water and aqueous solutions there is considerable scope for achieving such a reduction in the electrolysing voltage by reducing the hydrogen over-voltage at the cathode.

There have been many proposals of means of achieving such a reduction in hydrogen over-voltage.

For example, it is known that the hydrogen over-voltage at a cathode may be
20 reduced by increasing the surface area of the cathode, eg by etching the surface of the cathode in an acid, or by grit-blasting the surface of the cathode, or by coating the surface of the cathode with a mixture of metals, eg a mixture of nickel and aluminium, and selectively leaching one of the metals, eg aluminium, from the coating.

Other methods of achieving a low hydrogen over-voltage cathode which have
25 been described involve coating the surface of the cathode with an electrocatalytically-active material which comprises a platinum group metal and/or oxide thereof as mentioned in for example US 4,100,049 (wherein the coating is applied from an aqueous solution and then fired), GB 1,511,719 (wherein the coating is applied by
30 electroplating), Japanese Patent Publications Nos. 54090080 (wherein the coating is applied by sinter coating), 54110983 (wherein the coating is applied as a dispersion) and

53100036 and EP 0,129,374 (wherein the coating is applied in the form of salts which are then fired).

In our EP 0,546,714 there is described a cathode for use in an electrolytic cell which has a low hydrogen over-voltage when used in the electrolysis of water or aqueous solutions and which does not depend for its effectiveness on the presence of a coating containing a platinum group metal or oxide thereof. The cathode for use in an electrolytic cell disclosed in EP 0,546,714 comprises a metallic substrate and a coating thereon having at least an outer layer comprising a cerium oxide and at least one non-noble Group 8 metal wherein the cerium oxide provides at least 10% and preferably at least 20% by X-ray diffraction analysis of the outer layer.

We have now found surprisingly that cathodes for use in electrolytic cells may be prepared by the physical vapour deposition (PVD) on a suitable substrate of a coating comprising (a) cerium and/or cerium oxide and a non-noble Group 8 metal or (b) platinum and/or platinum oxide and ruthenium and/or ruthenium oxide. Furthermore, we have found that the durability of the cathode may be improved by a subsequent heat treatment.

The present invention provides an electrode, and a method for the preparation thereof, which (a) comprises a metallic substrate and a coating thereon which comprises an outer layer of good electrocatalytic activity and of uniform thickness which follows the contours of the surface of the substrate and (b) when used as a cathode in an electrolytic cell in which hydrogen is evolved at a cathode has an acceptable over-voltage and high durability.

According to the first aspect of the present invention there is provided a cathode which comprises a metallic substrate and a coating thereon comprising an outer layer which comprises an electrocatalytically-active material characterised in that (a) the outer layer is of substantially uniform thickness and (b) the contours of the surface of the outer layer are at least substantially the same as the contours of the substrate immediately underlying it.

In the cathode according to the present invention, the electrocatalytically-active material comprises (a) cerium and/or cerium oxide and at least one non-noble Group 8 metal or (b) platinum and/or platinum oxide and ruthenium and/or ruthenium oxide.

The cathode according to the present invention affords the advantages of an increased surface area for a given mass of electrocatalytically-active material and the more efficient use thereof to obtain a minimum thickness thereof.

Where the outer layer of the coating on the cathode according to the present invention contains cerium and/or cerium oxide we do not exclude the possibility that it may contain one or more other metals of the lanthanide series, eg lanthanum itself, that is some of the cerium may be replaced by one or more other lanthanide metals. However, where such other metal of the lanthanide series is present in the outer layer it should provide less than 2%w/w thereof and cerium should be present as the major amount of the total metal of the lanthanide series, including cerium.

Where the outer layer of the coating on the cathode according to the present invention comprises cerium and/or cerium oxide and a non-noble Group 8 metal the non-noble Group 8 metal may be iron, cobalt or preferably nickel. Often the outer layer of the coating comprises an intermetallic compound of cerium and a non-noble Group 8 metal, particularly nickel.

We are aware of certain prior disclosures in which the use of intermetallic compounds as low hydrogen over-voltage cathode coatings has been described, for example Doklady Akad Nauk SSSR 1984, Vol.276, No.6, pp1424-1426; Proceedings of a Symposium on Electrochemical Engineering in the Chlor-alkali and Chlorate Industries, The Electrochemical Society, 1988, p184-194; Journal of Applied Electrochemistry, Vol.14, 1984, pp107-115; and EP 0,089,141.

Where the outer layer of the coating on the cathode according to the present invention contains platinum and/or platinum oxide and ruthenium and/or ruthenium oxide it should contain 5-90 mole % platinum and preferably 10-80 mole % ruthenium.

The substrate of the cathode according to the present invention may comprise a ferrous metal, a film-forming metal or alloy thereof having properties similar thereto, eg titanium, or preferably nickel or an alloy thereof having properties similar thereto. However, it is often preferred that the substrate of the cathode is made of another material having an outer face of nickel or a nickel alloy. For example, the cathode may comprise a core of another metal, eg steel or copper, and an outer face of nickel or nickel alloy. Preferably the substrate comprises nickel or nickel alloy, such a substrate is corrosion resistant in an electrolytic cell in which aqueous alkali chloride solution is

electrolysed and cathodes according to the present invention which comprise a substrate of nickel or nickel alloy have long-term low hydrogen over-voltage performance.

The substrate of the cathode according to the present invention may have any desired structure. For example, it may be in the form of a plate, which may be foraminated, eg the cathode may be a perforated plate, or it may be in the form an expanded metal, or
5 it may be woven or unwoven. The cathode is not necessarily in plate form. Thus, it may be in the form of a plurality of so-called cathode fingers between which the anode of the electrolytic cell may be placed.

In the cathode according to the present invention the defined coating may be in
10 direct contact with the surface of the substrate. However, we do not exclude the possibility that the defined coating may be applied to an intermediate coating of another material on the surface of the substrate. Such an intermediate coating may be, for example, a porous nickel coating. However, the invention will be described hereinafter with reference to a cathode in which such an intermediate coating is not present.

15 According to a further aspect of the present invention there is provided a method for the preparation of an electrode according to the first aspect of the present invention which method comprises the steps of:

- (A) depositing the outer layer of the coating on the substrate by physical vapour deposition (PVD); and
20 (B) heating the product from Step A with the proviso that where the electrocatalytically-active material comprises cerium and/or cerium oxide the heating is carried out in a non-oxidising atmosphere.

As examples of PVD may be mentioned *inter alia* radio frequency (RF) sputtering, sputter ion plating, arc evaporation, electron beam evaporation, dc sputtering,
25 reactive PVD, etc or combinations thereof. It will be appreciated that where combinations of evaporation techniques are used in the same evaporation chamber in the PVD system separate targets may be used, for example a cerium target and a nickel target instead of, or in addition to, a cerium/nickel intermetallic target. By "target" we mean the material which is vapourised to produce a vapour for deposition on the
30 substrate in the PVD system.

In Step A of the method according to the present invention, the chamber in the PVD system may be charged with oxygen or ozone and/or an inert gas. Where an inert

gas is present in the chamber it is preferably argon. It will be appreciated that where the target in the PVD system is metallic and where it is desired to deposit an oxide, eg cerium oxide, platinum oxide or ruthenium oxide, an oxidising atmosphere is used in the PVD system.

5 The specific conditions used in Step A of the method according to the present invention may be found by the skilled man by simple experiment. For example, the pressure in the deposition chamber may be in the range 10^{-3} to 10^{-10} atmospheres.

 Where the target in the PVD system in Step A of the method according to the present invention is a cerium-containing intermetallic compound for the preparation of a
10 cathode as claimed in Claim 3 it will be appreciated that it must contain at least one non-noble Group 8 metal, ie at least one of iron, cobalt and nickel as well as cerium. Intermetallic compounds containing cobalt and/or nickel, particularly nickel, are preferred.

 The cerium-containing intermetallic compound, where it is used, may contain one
15 or more metals additional to cerium and a non-noble Group 8 metal but such other metals, where present, will generally be present in a proportion of not more than 2%.

 The cerium-containing intermetallic compound, where it is used, may have an empirical formula CeM_x where M is at least one non-noble Group 8 metal, x is in the range of about 1 to 5, and in which some of the cerium may be replaced by one or more
20 other lanthanide metals as hereinbefore described.

 Where a cerium-containing intermetallic compound is used as target in the PVD system in Step A of the method according to the present invention it may be a neat intermetallic compound, eg $CeNi_3$, or a mixture of intermetallic compounds, eg $CeNi_3$ and Ce_2Ni_7 , or an intimate mixture of a metal powder, preferably Ni, with an intermetallic, eg
25 Ce_2Ni_7 , to form, eg notionally $CeNi_{1.2}$, or a cerium/nickel alloy containing $CeNi_x$ phases wherein x is 1-5.

 Where a cerium-containing intermetallic compound is used as target in the PVD system in Step A of the method according to the present invention the concentration of cerium therein is typically not more than about 50% w/w and it is often preferred that it is
30 not less than about 10% w/w.

Where platinum and ruthenium metals are used as target in the PVD system in Step A of the method according to the present invention they may be present for example as a mixed bed or a disc.

5 In Step B of the method according to the present invention, the temperature to which the product from Step A is heated is preferably above 300°C and less than 1000°C and more preferably is about 500°C. The product from Step A is preferably heated for less than 8 hours and more than 0.5 hours and more preferably for at least one hour. The typical rate of heating is between 1°C and 50°C per minute and preferably is in the range 10-20°C/minute.

10 As examples of non-oxidising atmospheres which may be used in Step B of the method according to the present invention may be mentioned *inter alia* a vacuum, a reducing gas, eg hydrogen, or preferably an inert gas, eg argon, or mixtures thereof, eg heating in argon followed by vacuum treatment at elevated temperature.

15 Where the outer layer in the cathode according to the present invention comprises platinum and/or platinum oxide and ruthenium and/or ruthenium oxide the heating in Step B is typically carried out in air.

The precise temperature to be used in Step B of the method according to the present invention depends at least to some extent on the precise method by which the outer layer of the coating is deposited in Step A.

20 The mechanical properties and chemical/physical composition of the outer layer of the coating on the durable electrode according to the present invention are dependent on *inter alia* the length of time, the rate of heating and the temperature used in Step B.

The cathode according to the present invention may be a monopolar electrode or it may form part of a dipolar electrode.

25 The cathode according to the present invention is suitable for use in an electrolytic cell comprising an anode, or a plurality of anodes, a cathode, or plurality of cathodes, and optionally a separator positioned between each adjacent anode and cathode. The separator, where present, may be a porous electrolyte-permeable diaphragm or it may be a hydraulically impermeable cation permselective membrane.

30 The anode in the electrolytic cell may be metallic, and the nature of the metal will depend on the nature of the electrolyte to be electrolysed in the electrolytic cell. A

preferred metal is a film-forming metal, particularly where an aqueous solution of an alkali metal chloride is to be electrolysed in the cell.

The structure of the cathode, and of the electrolytic cell in which the cathode is to be used, will vary depending upon the nature of the electrolytic process which is to be carried out using the cathode. However, as the inventive feature of the present invention does not reside in the nature of the electrolytic cell nor of the cathode there is no necessity for the cell or the cathode to be described in any detail. Suitable types and structures of electrolytic cell and cathode may be selected from the prior art depending on the nature of the electrolytic process to be carried out in the cell. The cathode may, for example, have a foraminate structure, as in woven or unwoven mesh, or as in mesh formed by slitting and expanding a sheet of metal or alloy thereof, although other electrode structures may be used.

Prior to deposition of the coating on the substrate in the method according to the present invention the substrate may be subjected to treatments which are known in the art. For example, the surface of the substrate may be roughened, for example by sand-blasting, in order to improve the adhesion of the subsequently applied coating and in order to increase the real surface area of the substrate. The surface of the substrate may also be cleaned and etched, for example by contacting the substrate with an acid, eg an aqueous solution of hydrochloric acid, and the acid-treated substrate may then be washed, eg with water, and dried.

The present invention is further illustrated by reference to the accompanying drawing which represents by way of example only a micrograph of an electrode according to the present invention which may be prepared by the method according to the present invention.

In the drawing: Figure 1 is a micrograph of an electrode which may be prepared in Example 1.

In Figure 1, (1) is the electrode coating, (2) is the electrode substrate and (3) is the base on which the electrode was mounted for preparing the micrograph.

From Figure 1, it can be seen that the electrode coating (1) is of uniform thickness and that the contour of the surface thereof is substantially the same as the contour of the substrate immediately underlying it (2).

The present invention is further illustrated by reference to the following Examples.

EXAMPLES 1-2

These Examples illustrate cathodes according to the present invention.

5 General method

Nickel sheet was cleaned with acetone then grit-blasted with 60/80 alumina grit.

The sheet was mounted on a stainless steel plate (held with a nickel foil mask) and disposed in the PVD system which was allowed to pump down overnight.

The pressure in the PVD chamber was adjusted to 10^{-2} mbar by controlling the argon flow. A CeNi₃ powder target was presputtered for 2.5 hours at 500W incident RF power prior to use. The target shutter was removed and the powder target was sputtered for 60 hours whereupon a coating of nominal thickness 10 microns was obtained on the nickel substrate.

In Example 2, the cathode removed from the PVD chamber was subjected to a heat-treatment in argon at 500°C for 1 hour.

The cathodes prepared in Examples 1 and 2 were tested under the conditions described in EP 0,546,714. The results of the tests are shown in the Table.

TABLE

Example No.	Voltage saving over grit-blasted nickel/ mV after 6 days at 3kAm-2	Voltage saving over grit-blasted nickel/mV after 1 short
1	261	177
2	277	264
Hydrogen over-voltage of grit-blasted nickel is taken as 350mV		

From the Table it can be seen that the cathode from Example 1 has a low hydrogen over-potential whereas the cathode from Example 2 has both a low hydrogen over-potential and good durability.

CLAIMS

1. A cathode which comprises a metallic substrate and a coating thereon comprising an outer layer which comprises an electrocatalytically-active material characterised in that (a) the outer layer is of substantially uniform thickness and (b) the contours of the surface of the outer layer are at least substantially the same as the contours of the substrate immediately underlying it.
2. A cathode as claimed in Claim 1 wherein the electrocatalytically-active material comprises cerium and/or cerium oxide and at least one non-noble Group 8 metal.
3. A cathode as claimed in Claim 2 wherein the electrocatalytically-active material comprises an intermetallic compound of cerium and a non-noble Group 8 metal.
4. A cathode as claimed in Claim 2 or 3 wherein the non-noble Group 8 metal is nickel.
5. A cathode as claimed in Claim 1 wherein the electrocatalytically-active material comprises platinum and/or platinum oxide and ruthenium and/or ruthenium oxide.
6. A cathode as claimed in Claim 5 wherein the electrocatalytically-active material comprises 5-90 mole % platinum and 10-80 mole % ruthenium.
7. A method for the preparation of a cathode as claimed in Claim 1 which method comprises the steps of:
 - (A) depositing the outer layer of the coating on the substrate by physical vapour deposition (PVD); and
 - (B) heating the product from Step A with the proviso that where the electrocatalytically-active material comprises cerium and/or cerium oxide the heating is carried out in a non-oxidising atmosphere.
8. A method as claimed in Claim 7 wherein the target in the PVD system comprises an intermetallic compound of cerium and a non-noble Group 8 metal.
9. A method as claimed in Claim 8 wherein the non-noble Group 8 metal is nickel.
10. A method as claimed in Claim 7 wherein the PVD used in Step A is RF sputtering.
11. A method as claimed in Claim 7 wherein the PVD in Step A is carried out in an atmosphere comprising argon.
12. A method as claimed in Claim 7 wherein the non-oxidising atmosphere used in Step B comprises argon.

13. A method as claimed in Claim 7 wherein in Step B the product from Step A is heated at a temperature between 300°C and 1000°C.
14. An electrolytic cell wherein at least one cathode is a cathode as claimed in Claim 1 and/or prepared by a method as claimed in Claim 7.
- 5 15. A process for the electrolysis of water or an aqueous solution carried out in an electrolytic cell as claimed in Claim 14.

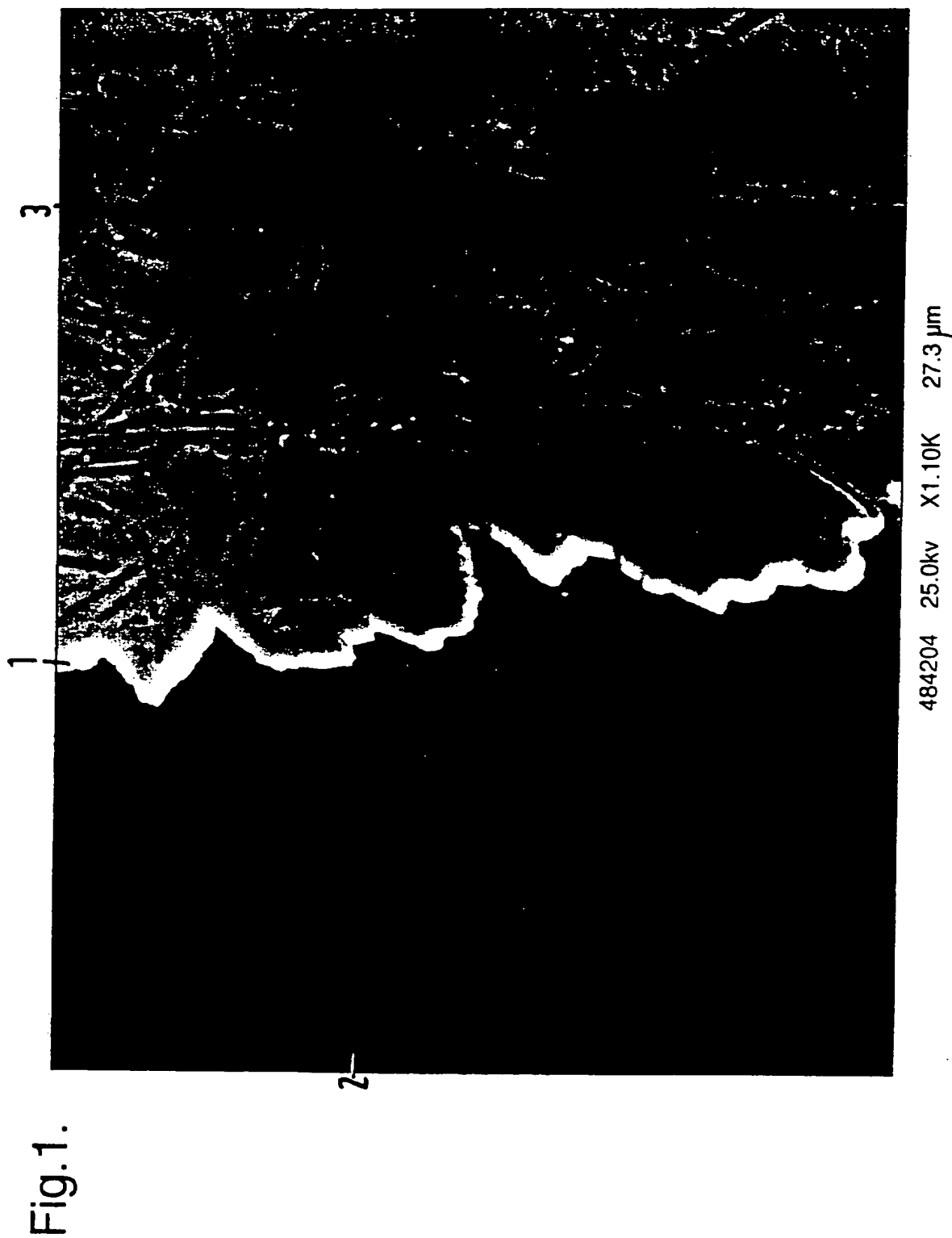
10

15

20

25

30



INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 96/00157

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C25B11/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C25B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 099 867 (ENERGY CONVERSION DEVICES, INC) 1 February 1984 see page 21, line 7 - page 22, line 13 see page 24, line 13 - page 26, line 15 see page 31, line 2 - line 4 see page 32, line 16 - line 22	1-3,7,8, 10,11, 14,15
Y	---	4,13
Y	EP,A,0 546 714 (IMPERIAL CHEMICAL INDUSTRIES PLC) 16 June 1993 see page 9; claims 1,4,6,14	4,13
A	GB,A,2 074 190 (JOHNSON MATTHEY & CO.) 28 October 1981 see page 4; example 2 ---	5,6
	--- -/-	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
 "E" earlier document but published on or after the international filing date
 "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
 "O" document referring to an oral disclosure, use, exhibition or other means
 "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

22 May 1996

Date of mailing of the international search report

07.06.96

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax (+31-70) 340-3016

Authorized officer

Groseiller, P

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 96/00157

C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE,A,43 19 951 (BASF) 22 December 1994 see page 7; example 1 see page 11; claims 5,7 -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 96/00157

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-99867	01-02-84	US-A- 4545883	08-10-85
		AU-B- 563946	30-07-87
		AU-B- 1679983	26-01-84
		CA-A- 1214453	25-11-86
		JP-B- 7033597	12-04-95
		JP-A- 59047391	17-03-84

EP-A-546714	16-06-93	AU-B- 656246	27-01-95
		AU-B- 2971192	17-06-93
		BR-A- 9204973	15-06-93
		CA-A- 2084811	14-06-93
		FI-A- 925636	14-06-93
		JP-A- 6179994	28-06-94
		US-A- 5492732	20-02-96
		US-A- 5324395	28-06-94
		ZA-A- 9209239	20-05-94

GB-A-2074190	28-10-81	AU-B- 537585	05-07-84
		AU-B- 6964181	29-10-81
		BE-A- 888507	17-08-81
		CA-A- 1201996	18-03-86
		DE-A- 3116032	18-02-82
		FR-A,B 2480795	23-10-81
		JP-C- 1512276	09-08-89
		JP-A- 57023083	06-02-82
		JP-B- 63061391	29-11-88
		NL-A- 8101934	16-11-81
		SE-B- 440240	22-07-85
		SE-A- 8102400	23-10-81
		US-A- 4414071	08-11-83

DE-A-4319951	22-12-94	BR-A- 9402435	24-01-95
		CA-A- 2125829	17-12-94
		EP-A- 0635587	25-01-95
		JP-A- 7305189	21-11-95
